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(54) Hair styling gels

(57) The invention provides hair styling gels containing a carboxylated polurethane resin, a viscosity enhancer, and an optional second hair fixative resin, in an aqueous carrier. The carboxylated polyurethane resin is hydrophilic and can be solubilized in water, or in a hydroalcoholic solution, in the absence of a base. The styling gel compositions impart excellent hair styling, conditioning, and hair set retention properties to treated hair.

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The present invention relates to hair styling gels that are applied to the hair to shape, style and condition the hair. In particular, the present invention relates to hair styling gels comprising a carboxylated polyurethane resin, an optional second hair fixative resin, a viscosity enhancer, and a carrier comprising water.

BACKGROUND OF THE INVENTION AND PRIOR ART

Hair styling gels are a convenient, easy-to-use form of hair styling composition, which may be applied by rubbing the gel manually on to wet or dry hair. The treated hair may then be set in a desired configuration, for example with a blow dryer.

The use of resins, or polymers, in hair styling compositions such as hair styling gels is well known. The resins typically used for these purposes are linear vinyl (e.g., an alkyl vinyl ether) or acrylic (e.g. an alkyl acrylate) polymers prepared by copolymerising two or more monomers in a free radical polymerisation reaction. The vinyl and acrylic-based resins are often used in relatively high concentrations in a hair styling composition to fix the hair in a particular configuration and to provide good hair set retention.

However, at high concentrations, the vinyl and acrylic-based resins exhibit disadvantages that adversely affect the hair, such as poor combing, poor feel, and excessive stiffness, crust and flaking. They are also incompatible with high water content systems - when incorporated in such systems they are prone to slow drying and tacky feel on the hair. Primarily these resins were designed for anhydrous alcohol hair spray compositions.

The disadvantages attributed to conventional vinyl and acrylic resins led investigators to search for new hair fixative resins that overcome these disadvantages. EP 0 619 111 A1 describes low VOC spray hair fixative compositions that are prepared from polyurethanes containing pendant free carboxyl groups. The polyurethane resins of EP 0 619 111 A1, however, require neutralisation with a base to make the polyurethane soluble in water or in a mixture of water and a polar organic solvent. Furthermore, there is no disclosure in EP 0 619 111 A1 of any gel-form hair fixative compositions.

SUMMARY OF THE INVENTION

The present invention provides a hair styling gel composition comprising:

(a) from 0.25% to 6% by weight of a carboxylated polyurethane resin,

(b) optionally, up to 6% by weight of a second hair fixative resin,

(c) from 0.01% to 3% by weight of a viscosity enhancer, and

(d) from 15% to 99.5% by weight of a carrier comprising water.

The hair styling gels impart good hair set retention and a soft, natural feel to treated hair, and provide superior hairstyle retention at high relative humidity. The hair styling gels also detangle and condition the hair. Such results are unexpected because traditional hair setting resins are hydrophobic. In contrast, the carboxylated polyurethane resins used in hair styling gels of the invention are hydrophilic, yet are adhesive to the hair and impart a soft, natural feel without being tacky.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

Carboxylated Polyurethane Resin

The hair styling gels of the present invention comprise about 0.25% to about 6%, preferably 0.5% to 5%, by weight of the composition, of a carboxylated polyurethane resin.

The carboxylated polyurethane resins are linear, hydroxyl-terminated copolymers having pendant carboxyl groups. They may be ethoxylated and/or propoxylated at least at one terminal end.

The carboxyl group can be a carboxylic acid group or an ester group, wherein the alkyl moiety of the ester group contains one to three carbon atoms.

The carboxylated polyurethane resin can also be a copolymer of polyvinylpyrrolidone and a polyurethane, having a CTFA designation PVP/polycarbamyl polyglycol ester.

The carboxylated polyurethane resins are soft and flexible, and typically have a melting point of about 40°C to about 120°C, preferably from 60°C to 100°C, most preferably from 70°C to 90°C.

Advantageously, the carboxylated polyurethane resins in the styling gels of the invention can be solubilized in water, or in a hydroalcoholic solution, in the absence of a base. Therefore, neutralisation with a base is not required to provide a useful hair styling gel.

A suitable carboxylated polyurethane resin for incorporation into the hair styling gel of the invention comprises a reaction product of :

(i) a diisocyanate,

(ii) an alkylene glycol or triol, and/or (iii) a diol component comprising a polymeric dihydroxy-terminated oligomer,

(iv) water, and

(v) a 2,2-di-(hydroxymethyl)-alkanoic acid.

An amine, such as diglycolamine, can be substituted for at least a portion of the water in the reaction mixture.

The diisocyanate component (i) can be an aliphatic or an aromatic diisocyanate, or a mixture thereof. An aliphatic diisocyanate is preferred.

Exemplary diisocyanates (i) include:

trimethylhexamethylene diisocyanate, isophorone diisocyanate, decamethylene-1, 10-diisocyanate, cyclohexane-1,2-diisocyanate, methylene bis(cyclohexyl-4-isocyanate), toluene-1,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, chlorophenylene diisocyanate, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, naphthalene-1,5-diisocyanate, l-methoxyphenyl-2,4-diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 3,3'-dichlorophenyl-4,4'diisocyanate, 2,2',5,5'-tetrachlorodiphenyl-4,4'-diisocyanate, trimethylhexamethylene diisocyanate, m-xylene diisocyanate, and mixtures thereof.

Suitable alkylene glycols or triols (ii) include low molecular weight glycols or triols, wherein the glycol or triol has at least two hydroxyl groups and a molecular weight up to about 200, for example ethylene glycol, diethylene glycol, propylene glycol, glycerol, hexylene glycol, cyclohexanediol, cyclohexanedimethanol, 1,4-butanediol, tripropylene glycol, triethylene glycol, dipropylene glycol, or mixtures thereof. These can be interacted with diisocyanate to provide a polyurethane.

Suitable diol components (iii) comprising a polymeric dihydroxy-terminated oligomer include polyoxyalkylene glycols having a molecular weight of about 200 to 20,000. Exemplary oligomers include polypropylene glycols, polyethylene glycols, ethylene glycol-propylene glycol copolymers, polybutylene glycols, and mixtures thereof. These can be interacted with diisocyanate to provide a polyurethane.

Preferably, a diisocyanate is interacted both with a low molecular weight diol or triol and with a polymeric dihydroxy-terminated oligomer to provide a polyurethane for use in the invention.

The carboxylated polyurethane resin contains pendant carboxyl groups and is hydrophilic. Preferably, the number of carboxyl groups is sufficient to give the carboxylated polyurethane resin an acid value of at least about 7 mg KOH/g resin (milligrams potassium hydroxide per gram of resin), since the hair styling gels of the invention then exhibit improved washability from the hair. Preferably the acid value of the carboxylated polyurethane resin in styling gels of the invention is from about 7 to about 50 mg KOH/g resin.

Examples of useful carboxylated polyurethanes are disclosed in Gould et al, US Patent No. 5,000,955. Other useful hydrophilic polyurethanes are disclosed in US Patent Nos. 3,822,238; 4,156,066; 4,156,067; 4,255,550; and 4,743,673.

One embodiment of the present invention is described as follows:

In this embodiment, the carboxylated polyurethane resin comprises a reaction product of:

a diol component comprising a polyoxyalkylene diol, preferably a polyoxyethylene diol having a number average molecular weight (M_n) of about 200 to about 20,000, a polyoxypropylene diol having an M_n of about 200 to about 2500, a block copolymer of ethylene oxide and propylene oxide having an M_n of about 1,000 to about 9,000, or a polyoxytetramethylene diol having an M_n of about 200 to about 4,000; about 0.01% to about 10% by weight of a low molecular weight alkylene glycol selected from the group consisting of ethylene glycol, propylene glycol, 2-ethyl-1,3-hexanediol, tripropylene glycol, triethylene glycol, 2,4-pentanediol, 2-methyl-1,3-propanediol, 2-methyl-1,3-pentanediol, cyclohexanediol, cyclohexanedimethanol, dipropylene glycol, diethylene glycol, and mixtures thereof; an organic diisocyanate; a 2,2-di-(hydroxymethyl)alkanoic acid; and water in an amount of about 0.01% to about 0.45% by weight of the reaction mixture, wherein the NCO/OH ratio (i.e., the R-value) is about 0.5 to about 1, and preferably about 0.6 to about 0.98. Most preferably, the R-value is about 0.65 to about 0.98.

In this embodiment, an amine can be used in the above reaction mixture for at least a portion of the water. The amine can be added to the reaction mixture in an amount of about 0.01% to about 0.8% by weight amine, preferably

about 0.02% to about 0.5% amine to about 0.01% to about 0.2% water in the reaction mixture. Amines that can be used in the reaction are ethylenediamine, propylenediamine, monoethanolamine, diglycolamine, and JEFFAMINE D1-230, D-400, D-2000, D-4000, ED-0600, ED-900, or ED-2001. The hydroxylamines and the JEFFAMINE products are manufactured by Texaco Chemical Company. Preferably, the amine is a hydroxylamine, and most preferably the amine is monoethanolamine and/or diglycolamine.

The polyoxyethylene diols are available from Union Carbide Corporation under the trademark CARBOWAX, such as CARBOWAX® 1450 AND CARBOWAX®8000 wherein the number represents number average molecular weight. The polyoxypropylene diols (PPG) are available from various sources, such as the PPG series of ARCO NIAX® PPG 1025, PPG 425, PPG 725, PPG 1225, and PPG 2025, and as R2134 (2200) and R2135 (4400), wherein the number represents number average molecular weight. Triols are also available from ARCO as NIAX® Polyols 11-34, LG-650, LG-56, LG-168, LHT-28, LHT-240. The polyoxytetramethylene diols are available from E.I. DuPont de Nemours as TERATHANE 600, 1000, 1400, 2000 and 2900. Polyetherpolycarbonate is available from BASF under the tradename polytetrahydrofuran 1000 CD and 2000 CD.

A block polyoxyalkylene polymer also can be used in the reaction referred to above. For example, a propylene oxide terminated block of ethylene glycol manufactured by BASF under the tradename PLURONIC R and a ethylene oxide terminated block of propylene glycol manufactured by BASF under the tradename of PLURONIC can be used for the polyoxyalkylene in the reaction. Examples of the block copolymers of the sequential addition of ethylene oxide and propylene oxide to ethylene diamine are made by BASF under the tradename of PLURONIC, such as PLURONIC F68, F64, F127, L35 L92, L82, 17R2, and 25R2.

Preferably, the polyoxyalkylene diol used in forming the polyurethane resin of this embodiment is polyoxyethylene diol. The blends of polyoxyalkylene diols contain at least about 10% polyoxyethylene diol, preferably, at least 20% polyoxyethylene diol, and most preferably, at least 25% polyoxyethylene diol, weight.

The amount of polyoxyalkylene diol having a molecular weight of 400 to 20,000 in the polyurethane resin can vary from about 10% to about 90%, preferably about 30% to about 90%, and most preferably about 40% to about 90%, by weight, and the number average molecular weight (M_n) of the polyoxyalkylene diol can vary from about 200 to about 20,000 preferably from about 800 to about 15,000, and more preferably from about 1000 to about 12,000.

The alkylene glycols are commercially available from several sources. For example, propylene glycol can be purchased from Aldrich Chemical Company as 1,2-propanediol. The amount of the alkylene glycol component in the polyurethane resin can be about 0.01% to about 20%, preferably about 0.05% to about 15%, more preferably about 0.1% to about 12%, still more preferably about 0.5% to about 10%, and most preferably about 1% to about 8%, by weight of the reaction mixture.

An especially preferred diisocyanate for this embodiment is methylene bis(cyclohexyl-4-isocyanate). Other examples of preferred diisocyanates are trimethyl hexamethylene diisocyanate, isophorone diisocyanate, methylene diisocyanate, hexamethylene diisocyanate, trimethylene diisocyanate, trimethylhexamethylene diisocyanate, cyclohexane-1,2-diisocyanate, and cyclohexane-1,4-diisocyanate. Also suitable are the isocyanate equivalents which form urethane linkages, exemplified by nitrile carbonates, such as adiponitrile carbonate disclosed in U.S. Patent No. 4,810,543. The amount of diisocyanate varies from about 3% to about 80%, such as from about 4% to about 70%, preferably from about 5% to about 60%, more preferably from about 6% to about 55%, and most preferably from about 6.5% to about 50%, by weight. The polyurethane resins are prepared by reacting the polyoxyalkylene diols with the diisocyanates.

The amount of water in the reaction mixture according to this embodiment is about 0.03% to about 0.40%, and more preferably about 0.05% to about 0.35%, by weight, of the reaction mixture.

The amount of 2,2-di-(hydroxymethyl)alkanoic acid in the reaction mixture is about 0.1% to about 8%, preferably about 0.3% to about 7%, and most preferably about 0.5% to about 6% by weight. Preferably, the 2,2-di(hydroxymethyl) alkanoic acid is dimethylolpropionic acid. The final reaction product has an acid value of at least about 0.2, preferably at least about 0.5, and most preferably at least about 1.

The ratio of NCO to OH groups from the diol, alkylene glycol, amines and water (i.e., the R-value) in the reaction mixture is about 0.5 to about 1, preferably about 0.6 to about 0.98, and most preferably from about 0.65 to about 0.98. The weight average molecular weight (M_w) of the carboxylated polyurethane resin is about 15,000 to about 300,000 preferably about 30,000 to about 200,000, and most preferably about 40,000 to about 190,000. The sum of all ingredients, including the diols, glycols, water and diisocyanate in the reaction mixture total 100% by weight.

The carboxylated polyurethane resin of the above described embodiment contains polyoxyalkylene units, i.e. soft segments, and/or alkylene units, i.e. hard segments, connected by urethane linkages. Preferably, the carboxylated polyurethane resin contains soft and hard segments. Also incorporated into the polymer chain is a small amount of diol having a pendant carboxyl group. The polymer chain further contains urea linkages resulting from a reaction between water and isocyanate groups, which modify the hair styling properties of the polyurethane.

Polyoxyethylene soft segments of the polyurethane resin impart hydrophilicity to the polyurethane. Soft segments derived from polyoxypropylene and polyoxytetramethylene diols provide a softer, but less hydrophilic, polyurethane. Hydrophilic polyurethane resins having improved strength and superior adhesive properties can be formed by using

combinations of polyoxyalkylene diols.

Another embodiment of the present invention is described as follows:

In this embodiment, the carboxylated polyurethane resin comprises a reaction product of:

a) a diol having a major portion of a polyoxyethylene diol having an M_n of 6,000 to 10,000 and a minor portion of a polyoxypropylene diol having an M_n of about 1,000 to about 3,500 or a polyoxyethylene diol having an M_n of about 600 to about 2000; b) an alkylene glycol; c) a diisocyanate; d) water in an amount of about 0.01% to about 0.45% by weight of the reaction mixture; and e) a 2,2-di(hydroxymethyl)-alkanoic acid, and an equivalent mole weight ratio of NCO to OH of the water, diol and glycol of about 0.6 to about 0.98. Preferably, at least 45% of the polyoxyethylene glycol of M_n about 8000, more preferably at least about 55%, still more preferably at least about 65%, and most preferably at least 75%, by weight, is used in the total reaction mixture. The amount of the lower molecular weight polyoxyethylene diol having an M_n of about 600 to about 2,000 is about 1% to about 15% and preferably from about 2% to about 10%, by weight of the reaction mixture. Preferably, the alkylene glycol is diethylene glycol, cyclohexanedimethanol, dipropylene glycol, or a mixture thereof.

The 2,2-di-(hydroxymethyl)alkanoic acid preferably is dimethylolpropionic acid. The amount of dimethylolpropionic acid is about 0.1% to about 8%, preferably about 0.3% to about 7%, and most preferably about 0.5% to about 6% by weight of the reaction mixture. The final product has an acid value of at least about 7 mg KOH/g resin, most preferably an acid value of about 7 to about 50 mg KOH/g resin. The sum of all ingredients, including the diols, glycols, water and diisocyanate in the above reaction mixture totals 100% by weight.

In this embodiment, an amine can be used in place of a portion of the water in the above reaction mixture. An amount of about 0.15% to about 0.6% amine, based on diglycolamine, is used with about 0.06% to about 0.5% of water, more preferably about 0.1% to about 0.4% of water, and most preferably of about 0.15% to about 0.3% of water.

The preferred diol according to this embodiment is a polyoxyethylene diol, preferably a polyoxyethylene diol of M_n about 6000 to about 10,000 alternatively with about 1% to about 10% of a polyoxyethylene diol of M_n about 600 to about 2,000. The preferred water level is about 0.03%, to about 0.4%, and most preferably about 0.05% to about 0.35% by weight.

The carboxylated polyurethane resins of the above embodiment are especially useful in hair setting compositions because the polyurethane resins are soluble in ethanol/water mixtures, and in dilute neutral to basic aqueous solutions. The polyurethane resins also impart improved feel and conditioning to treated hair, low flaking and crust, and improved set retention. These and other advantageous properties are observed when the carboxylated polyurethane resins are admixed with an optional second hair fixative resin, e.g., increased water solubility of the second hair fixative resin, improved feel of treated hair, and reduced crust and flaking.

For hair styling gels according to the present invention, the hydrophilicity of the polyurethane resin is an unexpected important property in combination with other desirable properties, such as washability. Conventional hair fixative resins are hydrophobic materials that impart a stiff feel to treated hair. The polyurethane resins in styling gels of the present invention are hydrophilic materials that give hair a soft, natural feel, yet are adhesive to the hair and impart excellent hair set retention.

It has also been found that the hair styling properties of the polyurethane resin in styling gels of the invention can be affected by small changes in the amount of water, the ratio of NCO/OH, and the amount of the di(hydroxymethyl) alkanoic acid in the reaction mixture.

Accordingly, in a further embodiment of the invention, the weight average molecular weight of the carboxylated polyurethane resins can be adjusted by modifying the amount of water in the reaction mixture within a predetermined range. The above-described polyurethane resins having an M_w of about 30,000 to about 75,000, and preferably about 35,000 to about 50,000; and a kinematic viscosity at 3 wt.% in 55/42 ethanol/water (by weight) of about 4 to about 40 centistokes (cs), are formed using about 0.1% to about 0.3% by weight water in the reaction mixture, and NCO/OH ratio (i.e., R-value) of about 0.75 to about 0.95, and about 0.5% to about 2.7% by weight of the reaction mixture of dimethylolpropionic acid.

A polyurethane resin having an M_w of about 55,000 to about 300,000 can be formed using about 0.3% to about 0.45% by weight water, a preferred NCO/OH ratio of about 0.75 to about 0.98, and about 0.5% to about 2.7% by weight dimethylolpropionic acid.

Polyurethane resins prepared using about 0.08% to about 0.45% by weight water in the reaction mixture, and an NCO/OH ratio of about 0.55 to about 0.95, preferably from about 0.6 to about 0.7, have a set retention at 30 minutes of about 80% to about 90%. An amount of water of about 0.15% to about 0.45% by weight in the reaction mixture and an NCO/OH ratio of about 0.6 to about 0.92, preferably from about 0.7 to about 0.9, can be used to provide polyurethane resins having a set retention of about 85% to about 98% at 30 minutes.

Alternatively, small amounts of diglycolamine can be substituted for the water in the reaction mixture, e.g., about 0.02% to about 1%, preferably from about 0.03% to about 0.75%, more preferably from about 0.04% to about 0.5%, and most preferably from 0.05% to about 0.4% by weight diglycolamine can be used in the reaction mixture.

The alkylene glycol used in th above-described embodiment can be, for example, ethylene glycol, diethylene

glycol, propylene glycol, dipropylene glycol, cyclohexanediol, 1,4-butanediol, cyclohexanedimethanol, tripropylene glycol, or triethylene glycol; preferably diethylene glycol, cyclohexanedimethanol, or dipropylene glycol; and most preferably diethylene glycol. The amount of the alkylene glycol (hard segments) in the reaction mixture is about 0.01% to about 20%, such as about 0.05% to about 15%, preferably about 0.1% to about 12%, more preferably about 0.5% to about 10%, and most preferably about 1% to about 5%, by weight.

In each of the above described embodiments, the polyurethane-forming reaction is catalysed by known catalysts. Tin-containing catalysts, such as tin salts or organotin esters, for example, stannous octoate and dibutyltin dilaurate, or tertiary amines, such as triethylene diamine and N,N,N',N'-tetramethyl-1,3-butane diamine, are preferred. The catalyst is used in an amount effective to catalyse the reaction, i.e., about .001 to 1 weight percent of the total weight of the reactive components. Reaction temperature is about 40°C to about 120°C.

In each of the above described embodiments, the carboxylated polyurethane resin contained carboxylic acid groups. However, carboxylated polyurethane resins wherein carboxylic acid groups are converted to ester groups with an alcohol having one to three carbon atoms also can be utilised as the carboxylated polyurethane resin in styling gels of the present invention.

Other useful carboxylated polyurethane resins are PVP/polycarbamyl polyglycol esters, which are copolymers of polyvinylpyrrolidone and polyurethane. These carboxylated polyurethane resins are available commercially from Phoenix Chemical, Inc., Somerville, NJ, as PECOGEL A-12, PECOGEL H-12, PECOGEL H-115 and PECOGEL H-1220.

Second Hair Fixative Resin

In addition to the carboxylated polyurethane resin, the hair styling gel may optionally contain up to about 6%, preferably from 0.25% to 5%, most preferably from 0.5% to 4% , by weight of the composition of a second hair fixative resin.

Preferably, the weight ratio of optional second hair fixative resin to carboxylated polyurethane resin in hair styling gels of the invention is about one or less.

The second hair fixative resin can be a nonionic, cationic, amphoteric or anionic resin, or a mixture of any of these. Advantageously the carboxylated polyurethane resin is compatible with each of these classes of resins.

The presence of a second hair fixative resin in hair styling gels of the present invention can, advantageously, reduce flaking attributed to the carboxylated polyurethane resins. In particular, the optional second hair fixative resin can impart a desired and predetermined degree of stiffness to the hair. The carboxylated polyurethane resin per se provides an elastic, flexible film on the hair, which gives the hair a soft, natural feel. However, consumers often equate a good hair setting composition with a degree of hair stiffness. The present hair styling gels, therefore, impart the desired stiffness to the hair, while further providing the benefits attributable to the polyurethane resin, such as conditioning, good style retention and good hair feel. By a judicious selection of the amount and nature of the second hair fixative resin, the hair styling gels of the invention can be designed to impart any desired feel to treated hair.

Examples of anionic hair fixative resins are copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers, terpolymers, etc., containing acrylic acid or methacrylic acid as the anionic radical-containing moiety and esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate, glycols having from 1 to 6 carbon atoms such as hydroxypropyl methacrylate and hydroxyethyl acrylate, styrene, vinyl caprolactam, vinyl acetate, acrylamide, alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide, and other compatible unsaturated monomers. One specific example is the emulsion polymerised terpolymer of methacrylic acid, n-butyl acrylate and ethyl acrylate (e.g., in a weight percent ratio of 31:42:27, respectively). Another specific example is Ultrahold® 8 (CTFA-Cosmetic, Toiletries and Fragrance Association designation of Acrylate/Acrylamide Copolymer).

Amphoteric polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl groups derived from monomers such as acrylic acid or methacrylic acid can also be used in the styling gels of the invention. One specific example of an amphoteric hairspray resin is Amphomer® sold by the National Starch and Chemical Corporation.

Examples of nonionic hair fixative resins are homopolymers of N- vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate and terpolymers of ethyl acrylate, butyl methacrylate and methyl methacrylate. Nonionic polymers containing N-vinylpyrrolidone in various weight average molecular weights are available commercially from ISP Corporation such as homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold by ISP (formerly GAF Corporation) under the tradename PVP K-90 and those

having an average molecular weight of about 1,000,000 sold under the trademark of PVP K-120.

Examples of cationic hair fixative resins are copolymers of amino-functional acrylate monomers such as lower alkyl aminoalkyl acrylate or methacrylate monomers such as dimethylaminoethyl methacrylate with compatible monomers such as N-vinylpyrrolidone, vinyl caprolactam, or alkyl methacrylates such as methyl methacrylate and ethyl methacrylate and alkyl acrylates such as ethyl acrylate and n-butyl acrylate.

Cationic polymers containing N-vinylpyrrolidone are commercially available from ISP Corporation such as those sold under the trademarks of Copolymer 845 and Copolymer 937 (copolymers of N-vinylpyrrolidone and t-butylaminoethyl methacrylate of average molecular weight about 1,000,000) and Gafquat® 755 and 755N (quaternary ammonium polymers formed by the reaction of dimethyl sulphate and a copolymer of N-vinylpyrrolidone and dimethylaminoethyl methacrylate of average molecular weight about 1,000,000).

Viscosity Enhancer

In addition to the carboxylated polyurethane resin and the optional second hair fixative resin, the hair styling gel of the invention contains about 0.01% to about 3%, preferably 0.1% to 2%, most preferably from 0.2% to 1.5%, by weight of the composition, of a viscosity enhancer.

The viscosity enhancer can be a gelling agent or a thickener, or any other compound capable of imparting a suitable gel-type viscosity to the composition. The identity of the viscosity enhancer is not critical, as long as the viscosity enhancer is compatible with the carboxylated polyurethane resin, and, if present, the second hair fixative resin, and does not adversely affect the stability or efficacy of the hair styling gel.

A suitable viscosity for a hair styling gel of the invention is about 10,000 up to about 100,000, preferably 20,000 to 100,000, most preferably 30,000 to 90,000 centipoise (as measured on a Brookfield Viscometer with a #6 spindle at 5 rpm). Lower viscosities, however, may be preferable if liquid gel- type formulations are desired.

Examples of viscosity enhancers include:

cellulose derivatives such as methylcellulose, hydroxymethylcellulose, hydroxyethyl cellulose, hydroxypropylcellulose, and hydroxypropyl methylcellulose;

water-soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose;

natural gums such as carrageenan, xanthan gum, gum arabic, gum tragacanth and guar gum and derivatives thereof such as hydroxypropyl guar and guar hydroxypropyl trimonium chloride;

inorganic thickeners such as colloidal magnesium aluminium silicate (Veegum), finely divided silica, natural clays such as bentonite and synthetic clays such as the synthetic hectorite available as Laponite(ex Laporte Industries Ltd);

vinyl-type polymeric thickeners such as polyvinylpyrrolidone, polyvinyl alcohol, sodium acrylate/vinyl alcohol copolymers and carboxyvinyl polymers, such as those polymers of acrylic acid crosslinked with about 0.75% to 2.0% of polyallylsucrose or polyallylpentaerythritol, obtainable under the Carbopol trademark from B.F.Goodrich.

Carrier

Hair styling gels of the invention also include from about 15% to about 99.5% by weight of the composition of a carrier comprising water. The carrier usually comprises up to about 98% water and may include other conventional liquid excipients suitable for personal care compositions, such as humectants, water-soluble or insoluble liquid emollients, organic liquid solvents and the like.

Suitable humectants include for example sorbitol, glycerine, propylene glycol, xylitol, polypropylene glycol and/or polyethylene glycol, and mixtures thereof. For "wet gel" type formulations, amounts of up to 50% by weight of the total composition of glycerol and/or polypropylene glycol may be employed. In clear gels where the refractive index is an important consideration, a suitable carrier is a mixture of about 20% to 80% of sorbitol with 0% to 80% glycerine and about 3% to 30% water.

Advantageously, it is not necessary to include a base in the water to neutralise and solubilize the carboxylated polyurethane resin. The carboxylated polyurethane resin also assists in solubilizing the optional second hair fixative resin.

Optional Ingredients

Hair styling gels of this invention may contain any other ingredient normally used in hair styling gels. These other ingredients may include emulsifiers such as anionic or nonionic surfactants, silicones, preservatives, colouring agents, chelating agents such as EDTA, antioxidants, fragrances, antimicrobials and sunscreens. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to about 5% by weight of the total composition.

Preferably, hair styling gels of this invention also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2%, preferably up to 1%, by weight of the total composition.

Among suitable hair care adjuvants, are:

(i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e. g. fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.

(ii) hair fibre benefit agents. Examples are:

- ceramides, for moisturising the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A preferred ceramide is Ceramide II, ex Quest. Mixtures of ceramides may also be suitable, such as Ceramides LS, ex Laboratoires Serobiologiques.

- fatty acids, for cuticle repair and damage prevention. Examples are branched chain fatty acids such as 18-methyleicosanoic acid, and other homologues of this series, straight chain fatty acids such as stearic, myristic and palmitic acids, and unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid and arachidonic acid. Particularly preferred are those fatty acids which occur naturally as essential, integral components of the hair fibre, and which therefore may need replenishing due to fibre damage and loss. The fatty acids may be added singly, as mixtures, or in the form of blends derived from extracts of e.g. lanolin.

The hair styling gels of the present invention are prepared by simply admixing and dissolving the polyurethane resin and the optional second hair fixative resin in an aqueous or hydroalcoholic carrier, with heating if necessary. Then, an aqueous solution of the viscosity enhancer and any optional ingredients is admixed with the aqueous solution of the hair setting resins to provide a homogeneous hair styling gel.

The invention will now be illustrated by the following nonlimiting Examples:

EXAMPLE A

PREPARATION OF A CARBOXYLATED POLYURETHANE RESIN A

A polyoxyethylene diol having an M_n of 8000 was heated under vacuum to 0.048% of water, than 744 parts of the dried diol was added to 21 parts diethylene glycol, 4.3 parts dimethylolpropionic acid, and 0.37 parts water. The resulting mixture was heated, with stirring, until a homogenous melt was obtained. Then, 88 parts methylene bis-cyclohexyl-4-4'-diisocyanate was added to the mixture. The NCO/OH ratio was about 0.98. When the temperature reached about 65°C, 2.25 ml of dibutyl tin dilaurate was added to the mixture, and the mass exothermed. The mass then was heated to 100°C, and held at 100°C for about one hour to complete polyurethane formation. The polyurethane resin had a weight average molecular weight (M_w) of 141,000. At 5% concentration, the polyurethane resin dissolved in 55/45 ethanol water to give a solution having a viscosity of 180 cps. At a concentration of 3%, in 60/40 propylene glycol/water, the solution had a viscosity of 5300 cps. A gel containg 19% of the polyurethane resin in 20/80 propylene glycol/water was tough, exceptionally clear and adhered to glass. The viscosity of the gel was reduced by raising the pH to about 7.0.

EXAMPLE B

PREPARATION OF POLYURETHANE RESIN B

A polyoxyethylene diol having an M_n of 8000 was heated under vacuum to 0.037% of water, then 744 parts of the dried diol was added to 21 parts diethylene glycol, 18.6 parts dimethylolpropionic acid, and 0.23 parts water. The resulting mixture was heated, with stirring, until a homogenous melt was obtained. Then, 115 parts methylene bis-cyclohexyl-4,4'-diisocyanate was added to the mixture. The NCO/OH ratio was about 0.98. When the temperature reached about 65°C, 2.25 ml dibutyl tin dilaurate was added to the mixture, and the mass exothermed. The mass was then heated to 100°C, and held at 100°C for about one hour to complete polyurethane formation. The polyurethane resin had an M_w of 63,000. At 5% concentration, the polyurethane resin dissolved in 55/45 ethanol water to give a solution having a viscosity of 1680 cps, and a reduced viscosity of 225 cps upon the addition of 2 ml ammonia to 180 grams of the solution. At a concentration of 3%, in 60/40 propylene glycol/water, the solution had a viscosity of 144 cps. A gel containing 19% of polymer in 20/80 propylene glycol/water was tough, exceptionally clear, and adhered to glass, displaying improved adhesive properties compared to gels made using a polyurethane without the alkanoic acid.

EXAMPLE C

PREPARATION OF A CARBOXYLATED POLYURETHANE RESIN C

Polyoxyethylene diol having an M_n of 8000 was heated under vacuum to 0.060% of water, and 736 parts of the dried diol was added to 21 parts of diethylene glycol, 18 parts of dimethylolpropionic acid, and .96 part of water. The mixture was heated with stirring until a homogeneous melt was obtained. Then, 114 parts of methylene bis-cyclohexyl-4-4'-diisocyanate were added. The NCO/OH ratio was 0.85. When the temperature reached about 63°C, 1.85 ml of dibutylin dilaurate was added, and the mass was allowed to exotherm. The mass was heated at 100°C for about one hour to complete formation of the polyurethane resin. The polyurethane resin dissolved in slightly basic 55/45 ethanol/water solution (wt/wt) at a concentration of 5 wt.% was clear and had a viscosity of 14 cps. The polyurethane resin had an M_w of 40,000 and was used in a hair styling aid to give a superior soft feel, excellent set retention, low crust, and low flaking properties to treated hair. The hair styling aid imparted a crust rating of 4.9, a feel of 6.7, a flaking rating of 7, a set retention of 97% at 30 minutes, and a set retention of 95% at 60 minutes to treated hair.

EXAMPLE D

PREPARATION OF POLYURETHANE RESIN D

Polyoxyethylene diol having an M_n of 8000 was heated under vacuum to 0.215% of water, and 736 parts of the dried diol was added to 21 parts of diethylene glycol, 59 parts of dimethylolpropionic acid, and 1.81 parts of water. The mixture was heated with stirring until a homogeneous melt was obtained. Then, 168 parts of methylene bis-cyclohexyl-4-4'-diisocyanate were added. The NCO/OH ratio was 0.65. When the temperature reached about 70°C, 1.85 ml of dibutyltin dilaurate was added, and the mass was allowed to exotherm. The mass was heated at 100°C for about one hour to complete formation of the polyurethane resin. The polyurethane resin had an M_w of 15,000 and dissolved in slightly basic 55/45 ethanol/water (wt/wt) solution at a concentration of 5 wt.% was clear and had a viscosity of 10 cps. The polyurethane resin had a kinematic viscosity of 4.60 cps in 55/42/3 ethanol/water/polymer solution by weight. The polyurethane resin was used in a hair styling aid to impart superior soft feel, excellent set retention, low crust, and low flaking properties to treated hair. The hair styling aid imparted a crust rating of 4.5, a feel of 4.5, a flaking rating of 1.8, and a set retention of 85% at 30 minutes to treated hair.

An important property of a hair styling gel is the ability to wash the hair setting resin from the hair, and thereby avoid polymer build-up on the hair. In accordance with an important feature of the present invention, the carboxylate polyurethane resin used in the hair styling gel can be removed from the hair by simply shampooing the hair. The unexpected washability of the hair styling gel is attributed to the hydrophilic nature of the polyurethane resin, and especially to the acid value of the carboxylated polyurethane resin. When the acid value of the hydrophilic polyurethane resin is at least about 7 mg KOH/g of resin, the polyurethane resin can be rinsed from the hair during shampooing without the need to neutralise the resin with an organic base.

The acid value is an indication of the number of pendant carboxylic acid groups on the polyurethane resin backbone. Although noncarboxylated polyurethane resins are hydrophilic, they are difficult to wash from the hair in a short time. Washability is enhanced by incorporating pendant carboxylic acid groups onto the polyurethane backbone.

The effect of acid value is illustrated in Table 1, wherein it is shown that washability is indep ndent of M_w or R-value, but varies with acid value. In effect, carboxylated polyurethane resins having an acid value of about 7 mg KOH/

g resin or greater, i.e., about 7 to about 50 mg KOH/g resin, had improved washability over resins having an acid value less than 7 mg KOH/g resin.

TABLE 1

PROPERTIES OF POLYURETHANE RESINS (R-VALUE = 0.73 TO 0.98)

Polyurethane Resin	R-value	Water	Acid Value[1]	Molecular Weight[2]	PDI[3]	Washability[4]
1	0.98	low	0.42	174,000	2.00	no
2[5]	0.98	low	2.28	141,000	2.00	no
3	0.84	low	8.01	28,000	2.00	yes
4[6]	0.98	low	8.28	63,000	2.00	yes
5	0.98	medium	0.50	188,000	2.20	no
6	0.85	medium	2.47	64,000	1.90	no
7	0.88	medium	7.87	30,000	1.60	yes
8	0.90	medium	7.70	43,000	1.80	yes
9	0.90	medium	8.04	39,000	1.70	yes
10	0.94	medium	7.78	39,000	1.80	yes
11	0.90	high	7.70	46,000	1.90	yes

1 The acid value was measured by titrating a solution of the resin with potassium hydroxide, the acid value is expressed in milligrams of KOH per gram of polyurethane;

2 The molecular weight is the weight average molecular weight (M_w) measured by size exclusion chromatography using polyethylene glycol calibration standards;

3 PDI is an abbreviation for "polydispersity index", i.e., the ratio [Weight average molecular weight]/[Number average molecular weight], which measures the relative spread in the molecular weight of the polyurethane resin;

4 The washability of the resin was determined by applying 3 wt.% solution of polyurethane resin onto clean, 2 gram, 6-inch long hair tresses, allowing the hair to dry, then washing the hair tresses with shampoo and warm water for about 3 minutes;

5 Polyurethane Resin A; and

6 Polyurethane Resin B.

To demonstrate the hair styling gels of the present invention, several styling gels were prepared. Each composition contained 0.5% to 2% by weight of a carboxylated polyurethane resin. The compositions of Examples 1-6 in Table 2 contained a polyurethane resin having an M_w of about 40,000 and a nonionic viscosity enhancer. The compositions of Examples 7-13 in Table 3 contained a carboxylated polyurethane resin having an M_w of about 15,000 and an anionic viscosity enhancer.

Each composition was prepared by dissolving the carboxylated polyurethane resin and the second hair fixative resin in a mixture of water and ethanol at 60°C. After cooling to room temperature, an aqueous solution of the viscosity enhancer was added to the resin solution, with mixing, until a homogeneous hair styling gel was provided.

TABLE 2

Example	1	2	3	4	5	6
D.I. Water	38.10[7]	37.85	38.25	37.75	38.05	38.05
Ethanol	10.00	10.00	10.00	10.00	10.00	10.00
Polyurethane Resin C[8]	0.75	0.75	0.75	0.75	0.75	0.50
D.I. Water	50.00	50.00	50.00	50.00	50.00	50.00
METHOCEL 40-100[9]	0.75	1.00				
VERSENE 100[10]	0.40	0.40				
NATROSOL 250[11]			1.00	1.50	1.00	1.00
Citric Acid (50%)					0.20	0.20
PVP K-120[12]						0.25
Total	100.00	100.00	100.00	100.00	100.00	100.00
Gel Appearance	clear	clear	clear	clear	clear	clear
Viscosity	viscous fluid	viscous fluid	viscous fluid	elastic, viscous fluid	elastic, viscous fluid	elastic, viscous fluid

7 percent by weight of the composition;

8 a carboxylated polyurethane resin having a molecular weight of about 40,000, as set forth in Example C;

9 METHOCEL 40-100 is a poly(hydroxypropyl methylcellulose) available commercially from Dow Chemical Co., Midland, MI;

10 VERSENE-100 is tetrasodium EDTA, an ion chelating agent available commercially from Dow Chemical Co.;

11 NATROSOL-250 is a hydroxyethyl cellulose polymer available commercially from Aqualon Co., Wilmington, DE; and

12 PVP K-120 is polyvinylpyrrolidone with K-value=120, as defined in "Kollidon" by Wolker Buhler, BASF, Ludwigshafen, Ch.2, 2nd edition (1993)

TABLE 3

Example	7	8	9	10	11	12	13
D.I. Water	25.00[7]	25.00	50.00	50.00	50.00	50.00	50.00
Ethanol	5.00	5.00					
Polyurethane Resin D[13]	2.00	2.00	2.00	2.00	2.00	2.00	2.00
D.I. Water	66.60	66.50	46.50	46.495	46.49	46.47	46.45
Carbopol, Ultrez[14]	0.40	0.50	0.50	0.50	0.50	0.50	0.50
TEA (50%)[15]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Polyacrylamide				0.005	0.01	0.025	0.05
Total	100.00	100.00	100.00	100.00	100.00	100.00	
Gel Appearance	sl.hazy	sl.hazy	sl.hazy	sl.hazy	sl.hazy	sl.hazy	sl.hazy
Viscosity	viscous	viscous	viscous	viscous	viscous	viscous	viscous
Tactile Property				stringy	stringy	stringy	stringy

13 a carboxylated polyurethane resin having an M_w of about 15,000, as set forth in Example D;

14 a polyacrylic acid available form B F Goodrich Co., Cleveland, O; and

15 triethanolamine, 50% in water

Examples 1-13 in Tables 2 and 3 show that hair styling gels containing a carboxylated polyurethane resin and a viscosity enhancer, and having a low VOC (e.g., 10% by weight or less), can be prepared. Tables 2 and 3 further show that a hair styling gel containing a low molecular weight polyurethane resin (e.g., about 15,000) or a high molecular weight polyurethane resin (e.g., about 40,000) can be prepared.

The hair styling gels also impart good hold and hair set retention to treated hair. For example, a hair styling gel containing a carboxylated polyurethane resin having an M_w of about 30,000 or greater provided equal or better set retention at 70% relative humidity than a control hair setting product containing the resin AMPHOMER. AMPHOMER is an acrylic copolymer resin and is widely used in commercial aerosol and pump hair spray products. Hair setting products containing AMPHOMER, therefore, were used as a control for comparison to hair setting compositions containing a polyurethane resin.

In tests designed to test the ability of a present hair styling gel to hold a hair set, hair styling gels containing 3 parts by weight carboxylated polyurethane resin and 0.5 parts by weight of a viscosity enhancer dissolved in a mixture of 10 parts by weight ethanol and 86.5 parts by weight water were prepared. The compositions were used in a test to determine the ability of the hair styling gel to maintain a hair set at 25°C and 70% relative humidity over a 24-hour period.

The set retention test measures the ability of a hair styling gel to hold or retain a hairstyle for an extended time at a particular relative humidity. Set retention was measured by applying 0.5 cc (cubic centimeters) of the hair styling gel to a one gram hair tress, and testing six tresses per composition. The sprayed tresses were allowed to dry overnight, at 30% relative humidity (i.e., RH), in a zigzag shape. The tresses were hung inside a humidity chamber at 25°C and a predetermined relative humidity (e.g., 70% RH). The relaxed length was recorded of the tresses and set retention was calculated using the equation:

$$\% \text{ Set Retention} = (L-L_t)/(L-L_o) \times 100,$$

wherein L is the length of the fully extended tress, L_o is the length of treated hair before relaxation, L_t is the length after exposure for a time, t. Six tresses were tested per hair styling gel composition and the data was statistically analysed and compared at the 95% confidence level. In all the experiments, AMPHOMER was used as the resin in a control hair setting product.

Hair set retention was measured at a low relative humidity (i.e., 70% RH) at 25°C. Table 4 summarises hair set retention tests from hair styling gels incorporating carboxylated polyurethane resins of different M_w. The hair set retention results were compared to the results provided by a control hair styling gel containing AMPHOMER. The comparative tests show that hair styling gels containing a carboxylated polyurethane resin having an M_w of about 30,000 or greater, e. g., about 30,000 to about 200,000, exhibited comparable or improved hair set retention over AMPHOMER. The hair set retention provided by the carboxylated polyurethane resins, therefore, is considered to be excellent because AMPHOMER is used in successful commercial hair setting compositions.

TABLE 4

HAIR SET RETENTION OF POLYURETHANE RESINS 25°C, 70% RELATIVE HUMIDITY

Polyurethane Resin	Molecular Weight (M_w)	%Set Retention, 30 min	% Set Retention, 1 hour	% Set Retention, 2 hours	% Set Retention, 24 hours
5	188,000	95.7	93.5	92.2	89.7
1	174,000	94.6	91.1	90.5	87.4
2[5]	141,000	95.0	90.8	90.0	84.7
6	64,000	90.2	83.5	81.3	75.4
4[6]	63,000	91.5	86.7	83.6	81.3
11	46,000	90.0	86.3	83.5	76.2
8	43,000	88.1	83.2	79.8	67.71
9	39,000	92.3	86.1	78.9	69.86
10	39,000	88.3	82.94	78.22	67.80
7	30,000	81.63	66.5	59.4	50.0
3	28,000	77.9	71.23	68.38	60.05
AMPHOMER[16]	not available	84.6	76.1	71.8	63.1

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16 AMPHOMER is a commercial hair fixative resin available from National Starch and Chemical Corp., Bridgewater, NJ and is an octylacrylamide/acrylates/butylaminoethylmethacrylate copolymer.

The following is another example of a hair styling gel of the present invention that was easily and uniformly applied to the hair, and exhibited good hair styling and hair set retention properties. The hair styling gel contains a hydrophilic copolymer of a polyurethane and polyvinylpyrrolidone. The hair styling gel is free of alcohol, and contains water as the sole component of the carrier.

Ingredients	% wt.
Deionised water	92.437
Carbomer[17]	0.403
Ammonium hydroxide	0.480
PECOGEL H-12[18]	6.680

17 CARBOPOL 940, a polyacrylic acid available commercially from B.F. Goodrich Co., Brecksville, O; and

18 PECOGEL H-12, a 12% by wt. copolymer of polyurethane and polyvinylpyrrolidone, distributed by Phoenix Chemicals Inc., Somerville, N.J.

Accordingly, a preferred hair styling gel contains a carboxylated polyurethane resin having a weight average molecular weight of about 30,000 to about 200,000. At a molecular weight below about 30,000, the carboxylated polyurethane resin has a reduced ability to hold the hair in a predetermined configuration for a sufficient time to meet consumer demands, unless a second optional hair fixative resin is present in the hair styling gel. If the molecular weight is greater than about 200,000, the hair styling gel can impart a tacky feeling to the hair. An optional second hair fixative resin also can be added to the hair styling gel to impart a desired degree of stiffness to treated hair.

A hair styling gel also possesses properties in addition to set retention in order to meet consumer demands. In particular, the present, consumer-acceptable hair styling gels impart a good feel to the hair and avoid excessive flaking and crust. Hair styling gels that provide natural, or reduced, crusts are desired. Hair crust is tested subjectively in this test wherein a group of trained judges evaluate hair tresses treated with a hair styling gel. The hair flaking test measures the amount of flakes or dust that form on the hair after combing hair that has been treated with the compositions and dried. The present hair styling gels imparted a consumer acceptable feel to treated hair, and the crust and flaking was within acceptable limits.

Claims

1. A hair styling gel composition comprising:

   (a) from 0.25% to 6% by weight of a carboxylated polyurethane resin,

   (b) optionally, up to 6% by weight of a second hair fixative resin,

   (c) from 0.01% to 3% by weight of a viscosity enhancer, and

   (d) from 15% to 99.5% by weight of a carrier comprising water.

2. A composition according to claim 1 in which the carboxylated polyurethane resin has a weight average molecular weight of 30,000 to 200,000.

3. A composition according to claim 1 or 2 in which the carboxylated polyurethane resin comprises a reaction product of a mixture comprising:

   (i) 10% to 90% by weight of the mixture of a polyoxyalkylene diol having a numb r av rage molecular weight

of 200 to 200,000;

(ii) 0.01% to 20% by weight of the mixture of an alkylene glycol;

(iii) 3% to 80% by weight of the mixture of an organic diisocyanate;

(iv) 0.1% to 8% by weight of the mixture of a 2,2'-di (hydroxymethyl)alkanoic acid; and

(v) 0.01% to 0.45% by weight of the mixture of water,

wherein the ratio of isocyanate groups to hydroxyl groups is from 0.5 to 1.

4. A composition according to claim 3, in which the polyoxyalkylene diol is selected from the group consisting of polyoxyethylene diols having a number average molecular weight of from 200 to 20,000, polyoxypropylene diols having a number average molecular weight of from 200 to 2,500, polyoxytetramethylene diols having a number average molecular weight of from 200 to 4,000, block copolymers of ethylene oxide and propylene oxide having a number average molecular weight of 1,000 to 9,000, and mixtures thereof.

5. A composition according to claim 3 or 4, in which the alkylene glycol is selected from th group consisting of ethylene glycol, propylene glycol, 2-ethyl-1,3-hexanediol, tripropylene glycol, triethylene glycol, 2,4-pentanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, cyclohexanediol, cyclohexanedimethanol, glycerol, hexylene glycol, 2-methyl-1,3- pentanediol, dipropylene glycol, diethylene glycol, and mixtures thereof.

6. A composition according to any one of claims 3 to 5, in which the organic diisocyanate is an aliphatic diisocyanate selected from the group consisting of methylene bis(cyclohexyl-4-isocyanate), trimethylhexamethylene diisocyanate, isophorone diisocyanate, tetramethylene-1,4-diisocyanate, hexamethylene diisocyanate, trimethylene diisocyanate, cyclohexane-1,2-diisocyanate, decamethylene-1,10-diisocyanate, cyclohexane-1,4-diisocyanate, and mixtures thereof.

7. A composition according to any one of claims 3 to 6, in which the 2,2-di (hydroxymethyl) alkanoic acid comprises dimethylolpropionic acid.

8. A composition according to claim 1, in which the carboxy groups of the carboxylated polyurethane resin comprise carboxylic acid groups, ester groups, or a mixture thereof.

9. A composition according to claim 1, in which the carboxylated polyurethane resin comprises a PVP/polycarbamyl polyglycol ester.

10. A composition according to any one of claims 1 to 9 which is free of a neutralizing agent for the carboxylated polyurethane resin.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 6235

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 42 25 045 A (BASF AG) * claim 1; examples D,E *	1	A61K7/06
A	DE 44 38 849 A (HENKEL KGA) * example 1 *	1	
A,D	EP 0 619 111 A (NATIONAL STARCH AND CHEM. I.H.C.)	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

A61K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 February 1998	Glikman, J-F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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